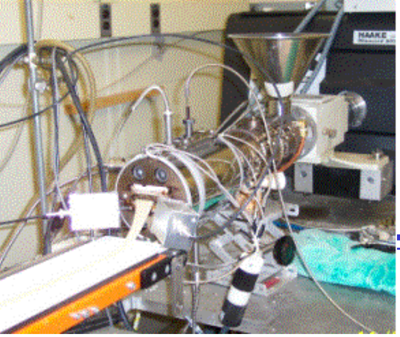
Multifunctional Monitoring of Polymer/Clay Compounding Using Dielectric, Optical and Fluorescence Measurements

Anthony J. Bur, Yu-Hsin Lee, Steven C. Roth and Paul R. Start
NIST, Polymers Division

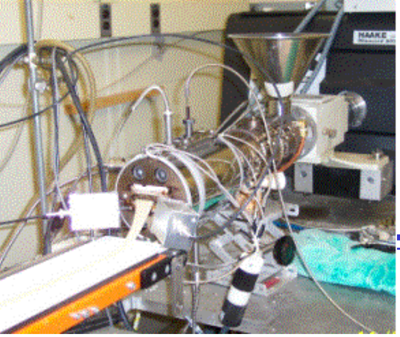
and

Paul H. Maupin
Office of Basic Energy Science, US Dept.of Energy



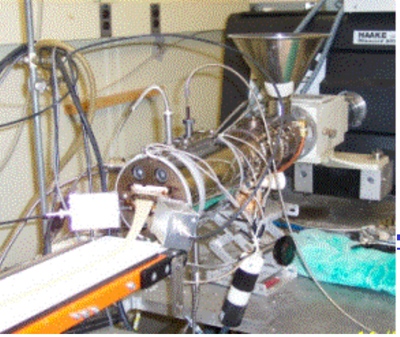
Outline

- ✓ **The NIST Dielectric Slit Die**
- ✓ **Monitoring Nylon/Clay Nanocomposites Compounding**
  - **Dielectric**
  - **Optical transmission**
  - **Fluorescence**



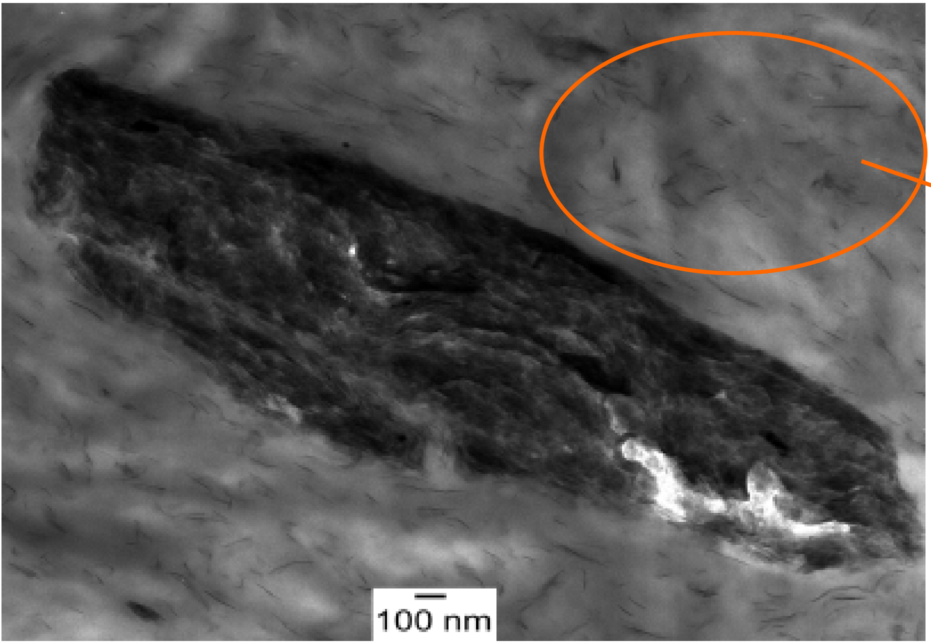
Outline

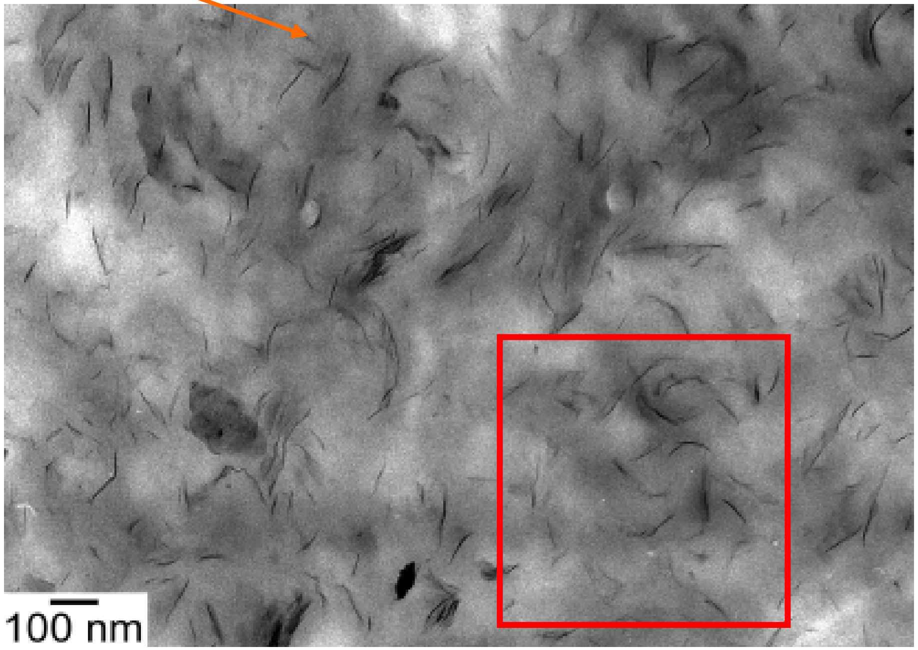
- ✓ **The NIST Dielectric Slit Die**
- ✓ **Monitoring Nylon/Clay Nanocomposites Compounding**
  - **Dielectric**
  - **Optical transmission**
  - **Fluorescence**
- ✓ **Model Development: Extent of Exfoliation**

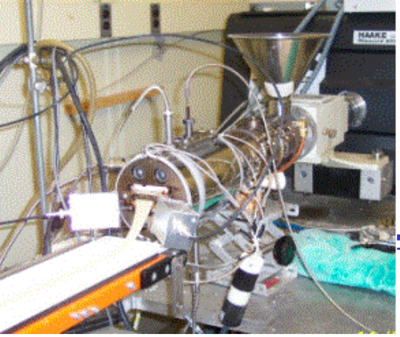


Outstanding Question:
What is an exfoliated clay nanocomposite?

Nylon 6/30B clay



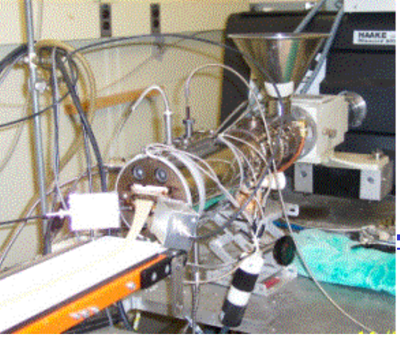




Exfoliation is the Goal

Enhanced resin-filler interface surface area yields:

- **Improved materials properties of composites with less filler material**
- **Improved mechanical properties**
  - **modulus, strength, toughness**
  - **applications: automotive, packaging**
- **Improved barrier resin behavior**
- **Improved fire retardation**

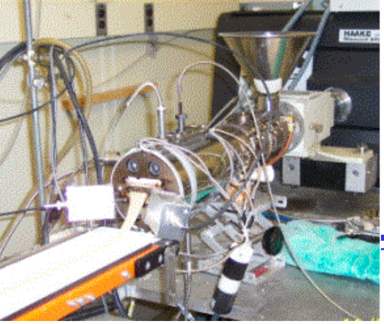


Exfoliation is the Goal

Enhanced resin-filler interface surface area yields:

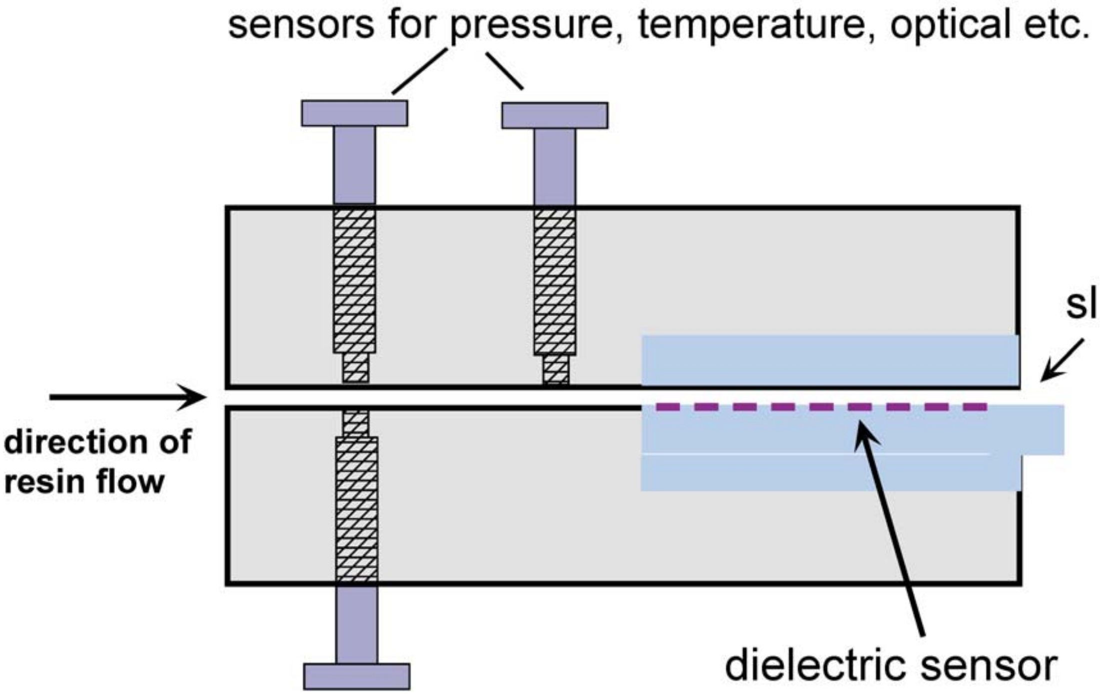
- **Improved materials properties of composites with less filler material**
- **Improved mechanical properties**
  - **modulus, strength, toughness**
  - **applications: automotive, packaging**
- **Improved barrier resin behavior**
- **Improved fire retardation**

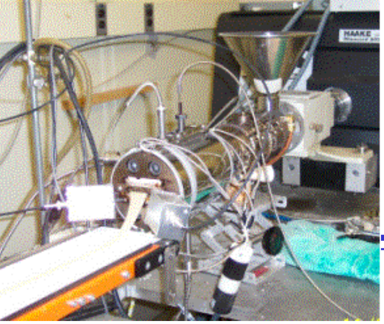
In order to control exfoliation, you must first measure it.



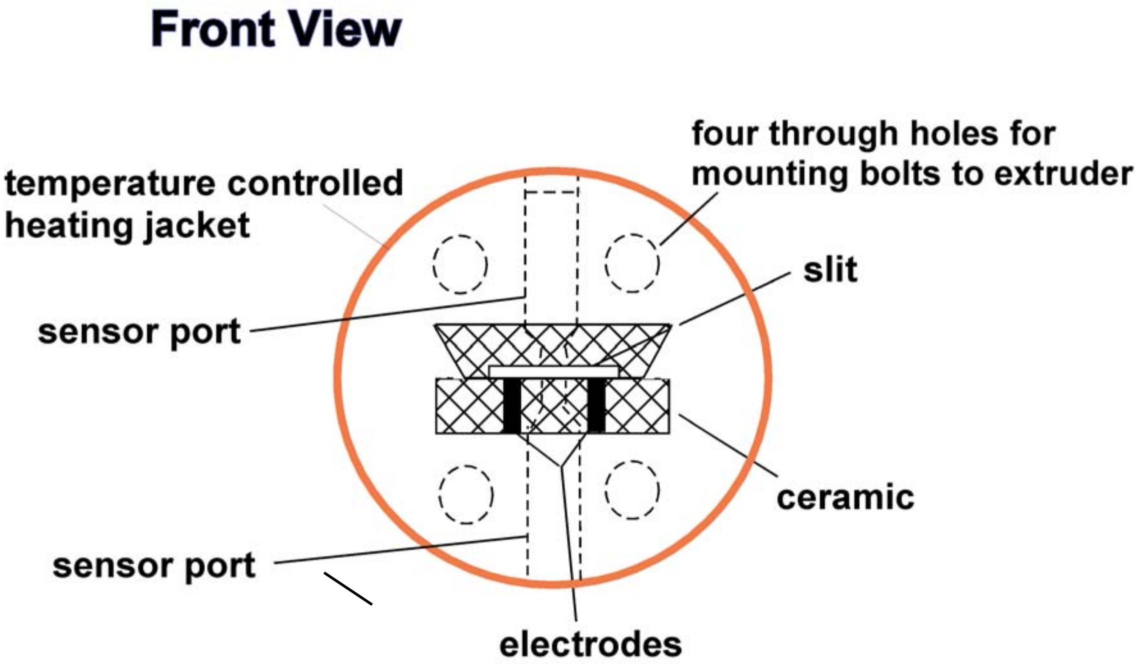
The NIST Dielectric Slit Die

Instrument Concept:
A Slit Platform for Mounting Multiple Sensors



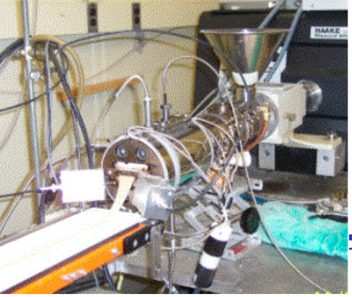


The NIST Dielectric Slit Die



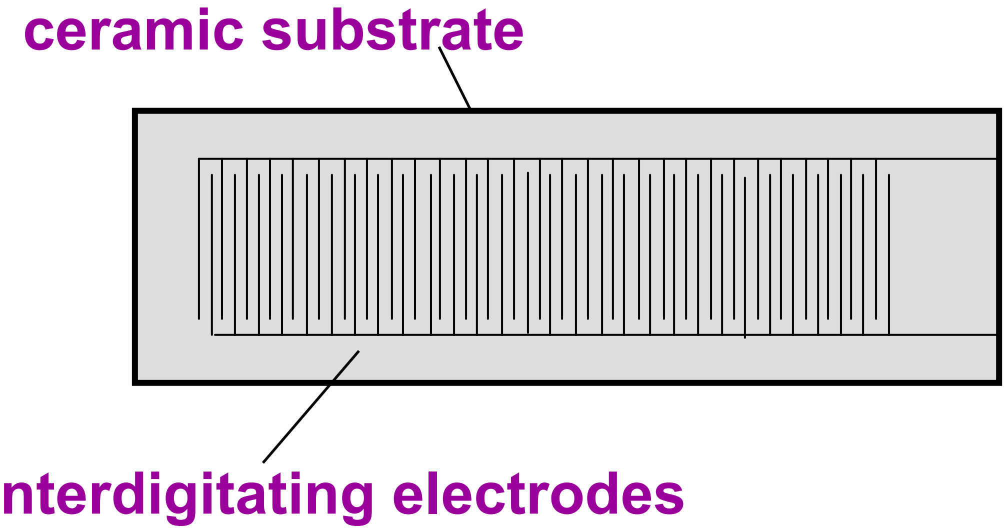
Advantage of the slit configuration:

- **Constant geometry sample chamber can be interrogated by multiple of sensors**
- **Has configuration of a slit die rheometer.**

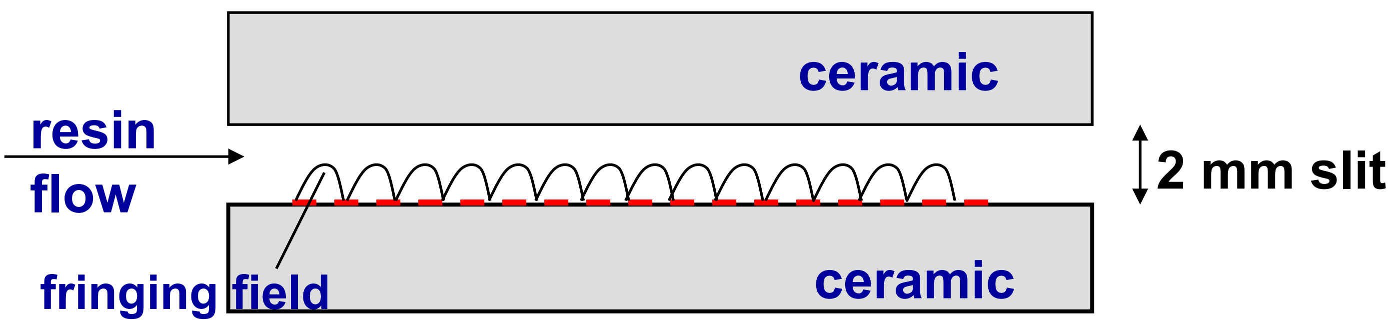


Interdigitating Electrodes

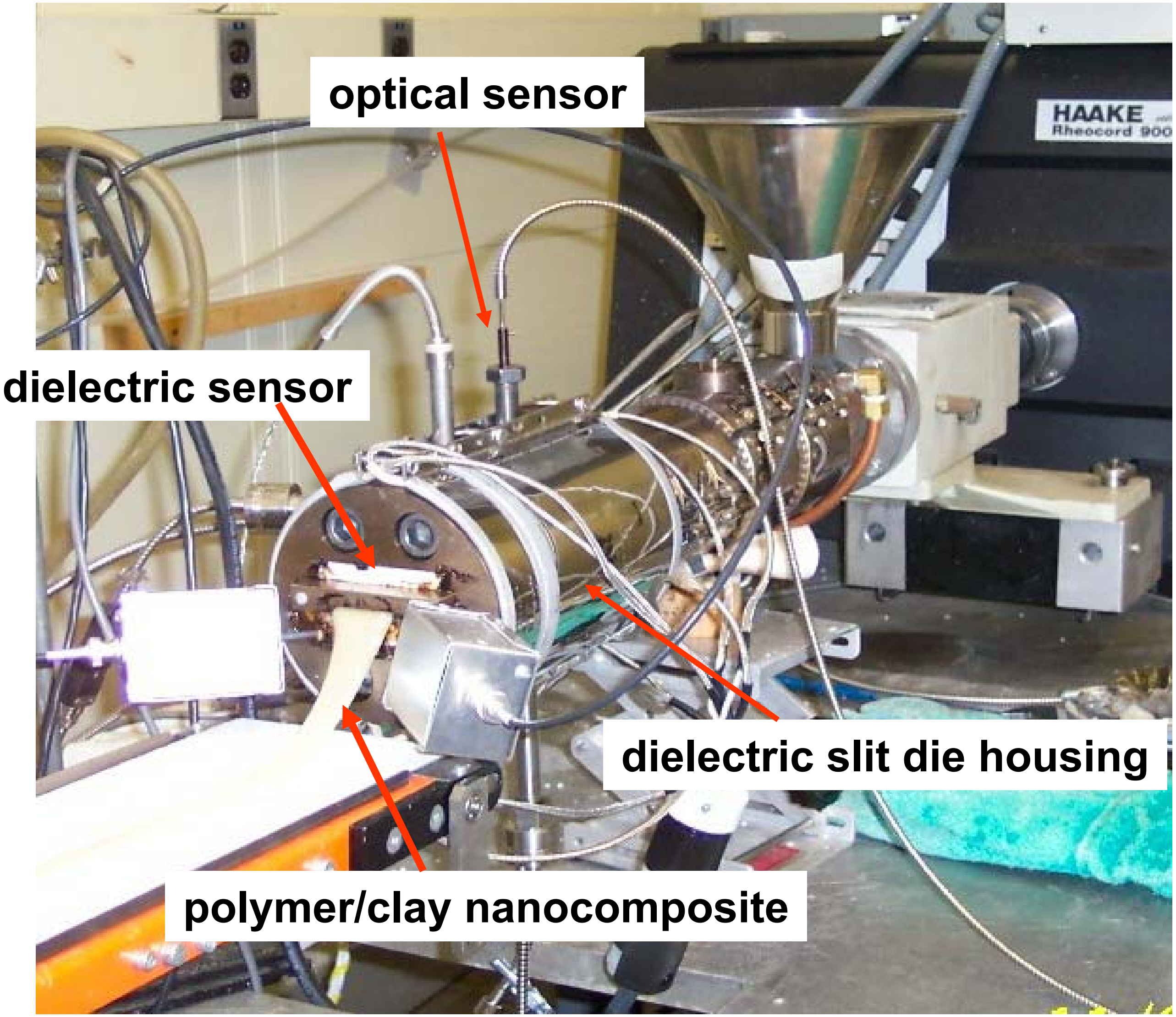
Top View

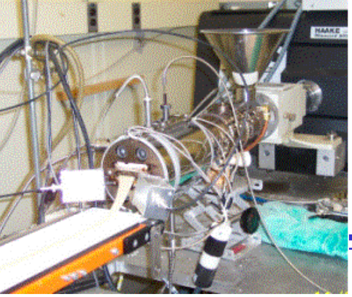


Side View

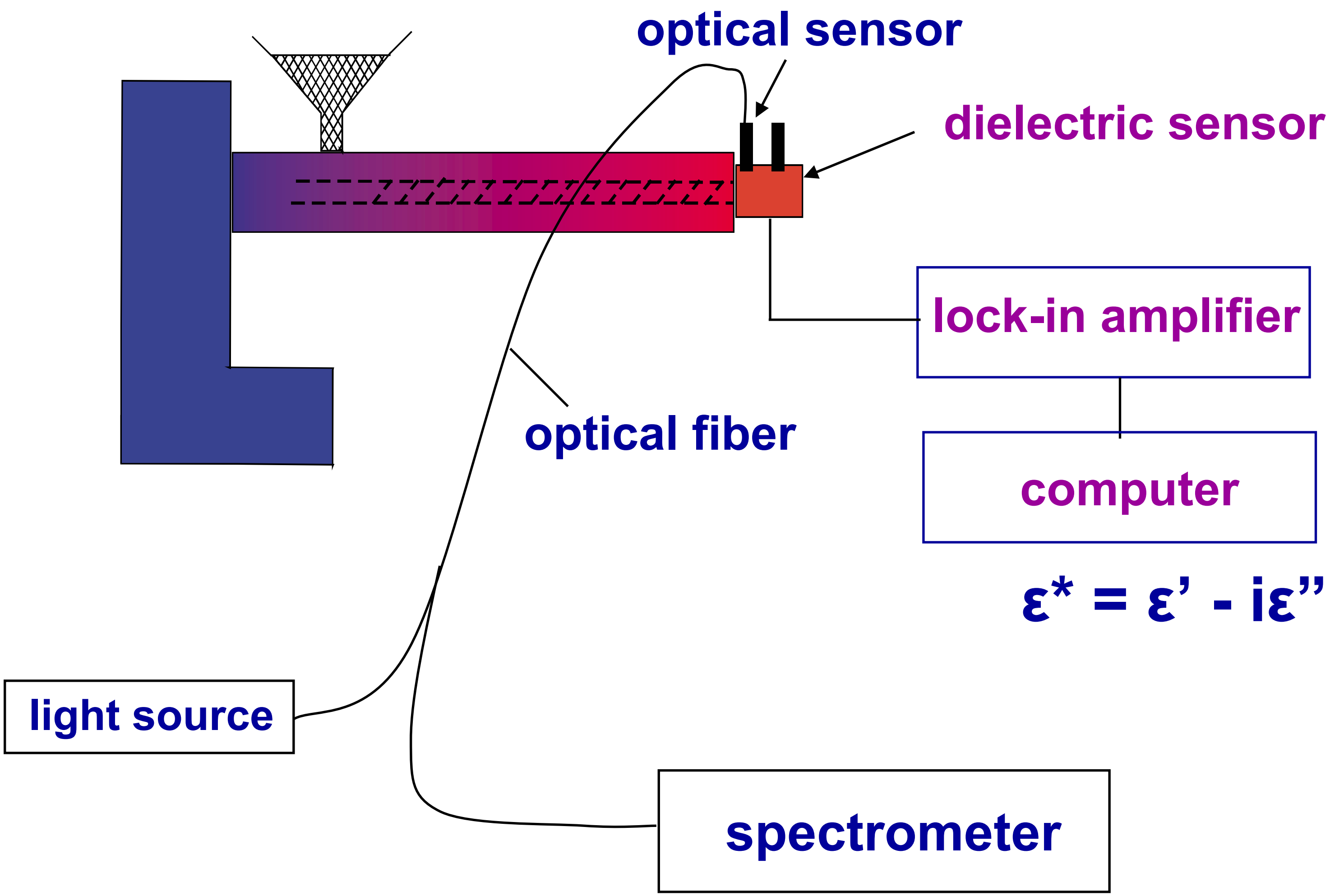


The NIST Dielectric Slit Die

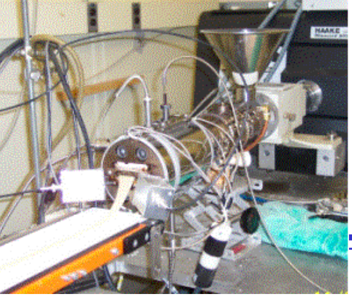




Experimental Setup for Extrusion



$$\varepsilon^* = \varepsilon' - i\varepsilon''$$

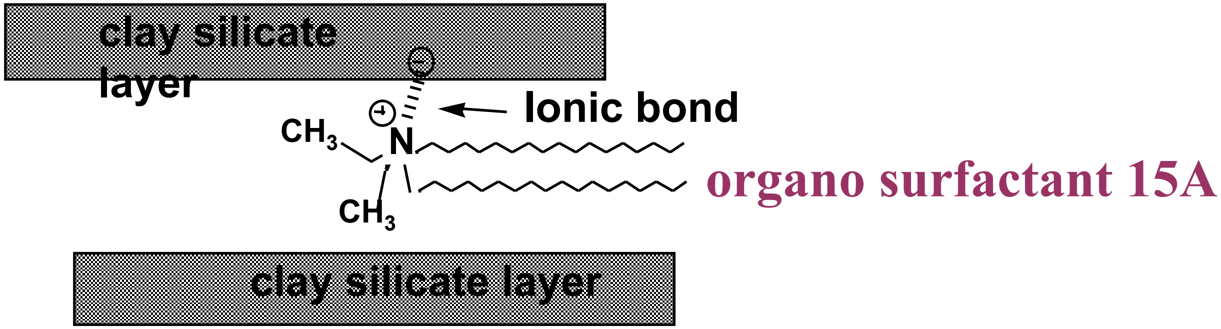


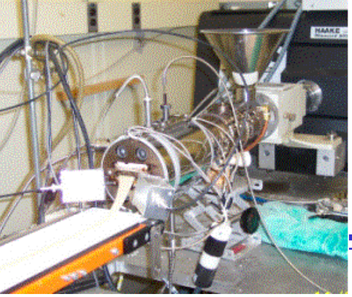
Compounding Nylon/Clay Composites

Materials:

- **nylon 11 and Nylon 6**
- **montmorillonite clays**
  - **natural Na+ clay (aggregate composite)**
  - **three organo modified clays**

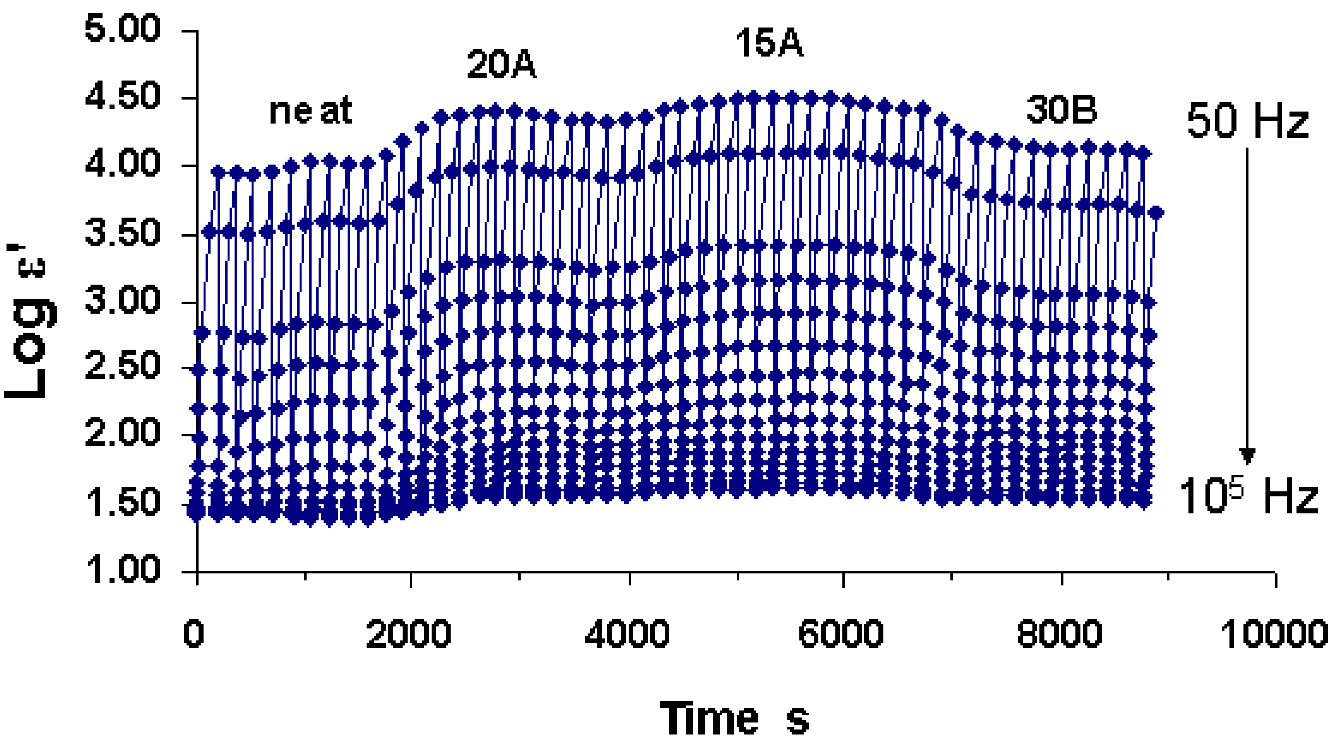
    15A, 20A, 30B (partially exfoliated)

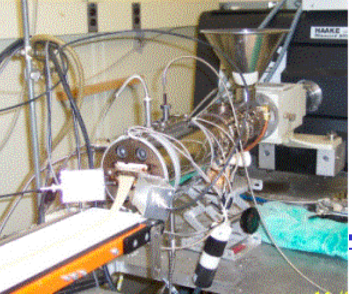




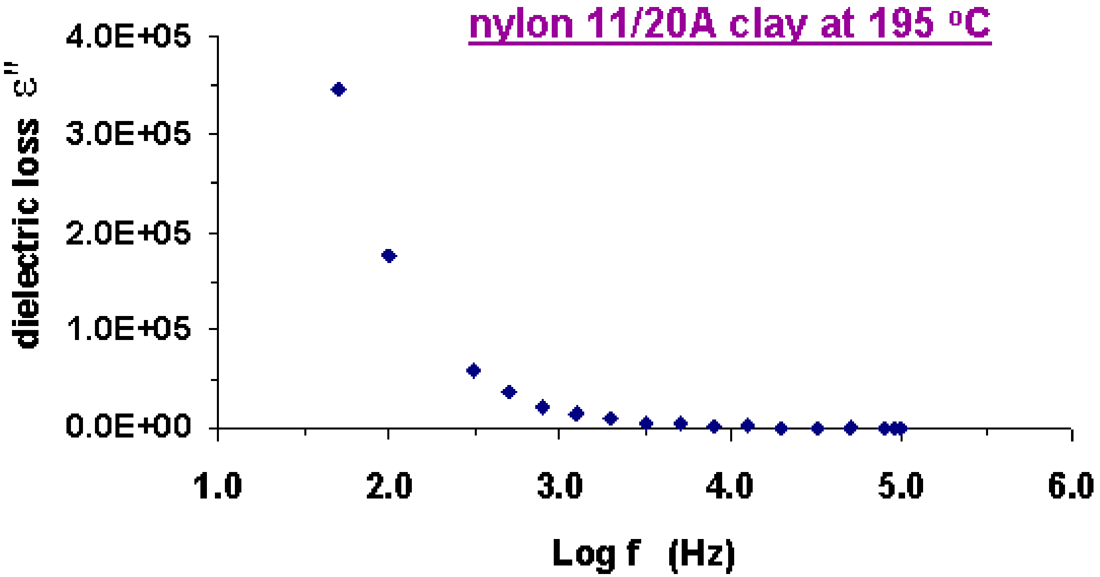
Compounding Nylon/Clay Composites: Dielectric Monitoring

nylon 11 at 195 °C





Analyzing Dielectric Data

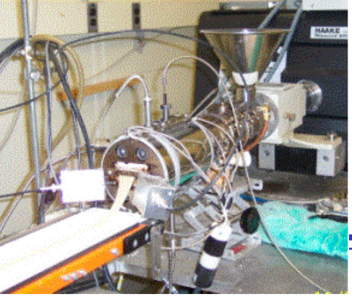


Data are fit with dispersion function:

$$\varepsilon^* = -\underbrace{\frac{i\sigma}{\omega\varepsilon_o}}_{\text{DC conductivity}} + \underbrace{\varepsilon_\infty + \sum_j \frac{(\varepsilon_o - \varepsilon_\infty)_j}{\left[1 + (i\omega\tau_j)^{1-\alpha_j}\right]}}_{\text{Cole-Cole dielectric relaxation}}$$

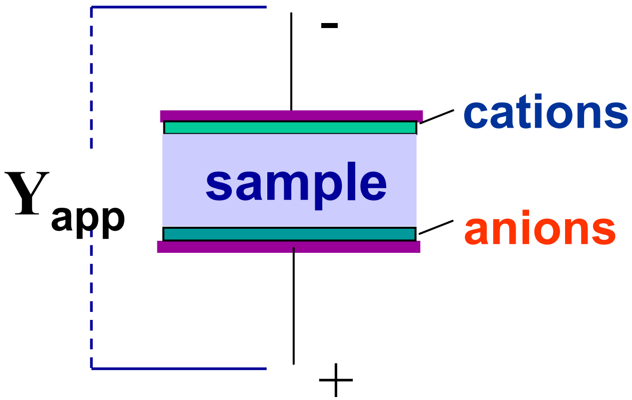
DC conductivity

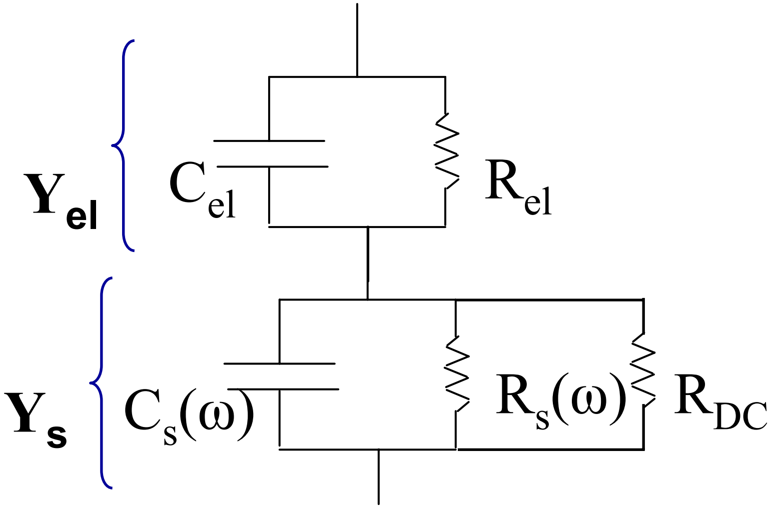
Cole-Cole dielectric relaxation

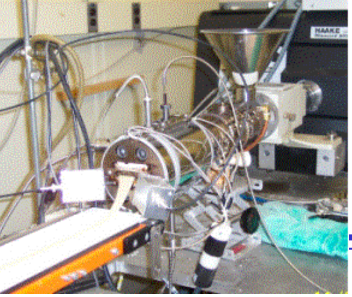


Analyzing Dielectric Data

Electrical impedance model:

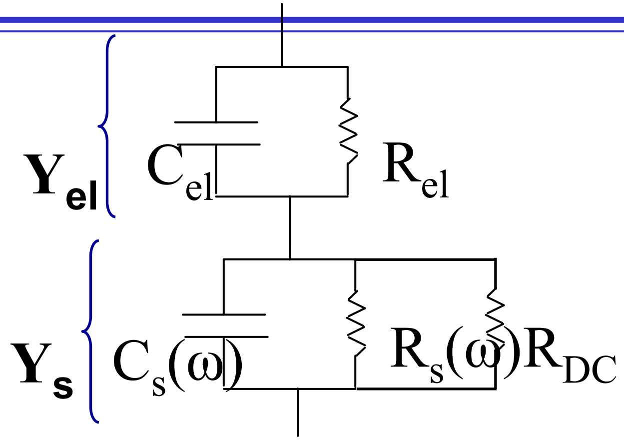






Analyzing Dielectric Data

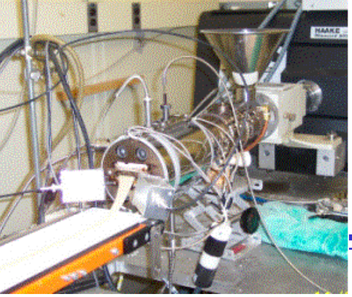
Electrical impedance model:



$$\varepsilon^* = -\frac{i\sigma}{\omega\varepsilon_o} + \varepsilon_\infty + \sum_j \frac{(\varepsilon_o - \varepsilon_\infty)_j}{\left[1 + (i\omega\tau_j)^{1-\alpha_j}\right]}$$

DC conductivity

Cole-Cole dielectric relaxation



Analyzing Dielectric Data

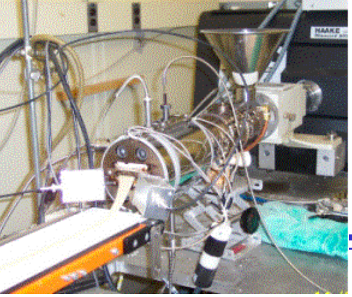
$$\varepsilon^{*} = -\frac{i\sigma}{\omega\varepsilon_{o}} + \varepsilon_{\infty} + \sum_{j} \frac{\left(\varepsilon_{o} - \varepsilon_{\infty}\right)_{j}}{\left[1 + \left(i\omega\tau_{j}\right)^{1-\alpha_{j}}\right]}$$

DC conductivity

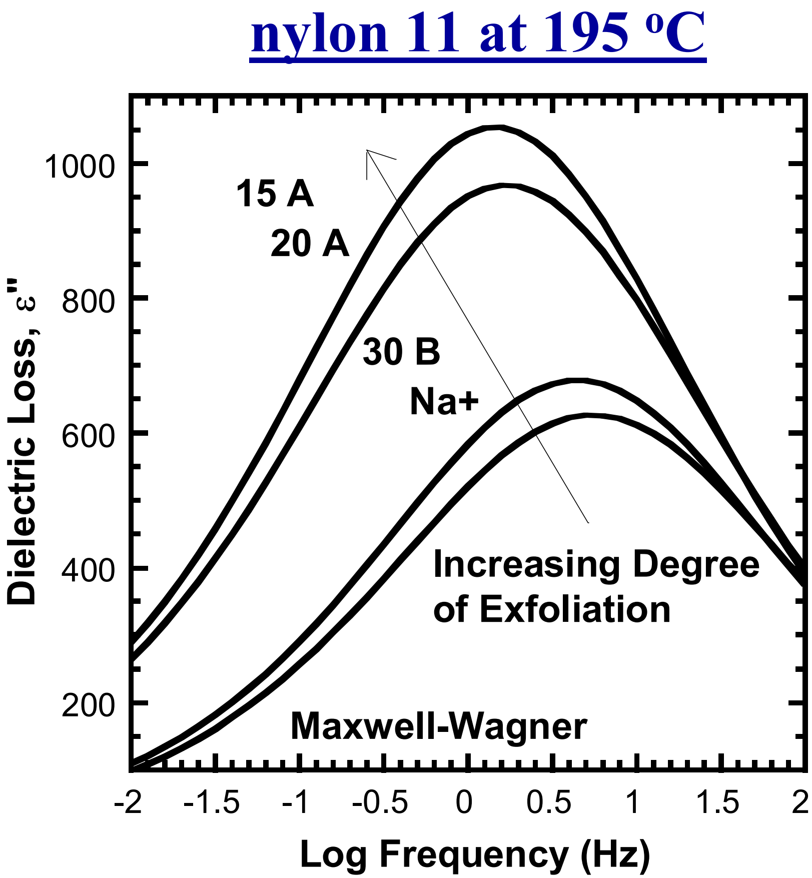
Cole-Cole dielectric relaxation

Analysis protocol:

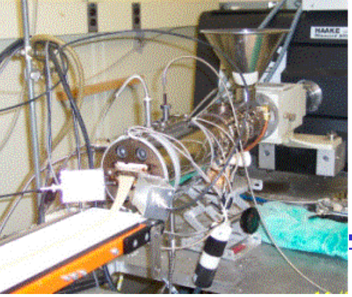
- Examine raw data for relaxation phenomena
  noting magnitude and position on frequency scale
- Carry out non-linear regression curve fitting
  to retrieve relaxation parameters



Maxwell Wagner Relaxation

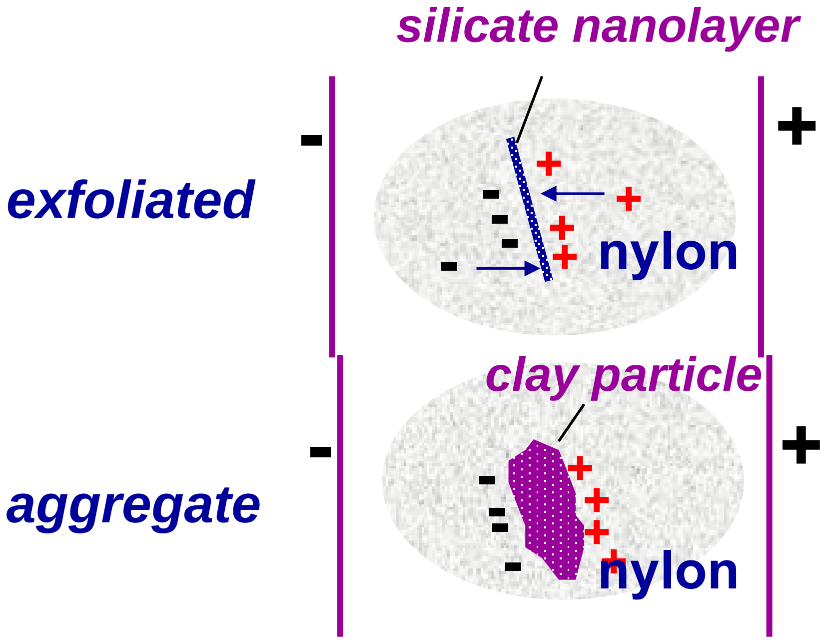


	Log f_{MW}
Nylon 11 at 198 °C	--
Nylon 11/Na+	0.74
Nylon 11/30B	0.62
Nylon 11/20A	0.24
Nylon 11/15A	0.16
Nylon 6 at 242 °C	--
Nylon 6/15A	1.98
Nylon 6/30B	1.10



Maxwell Wagner Relaxation

Reflects RC Time Constant for Charging Polymer/Clay Interface

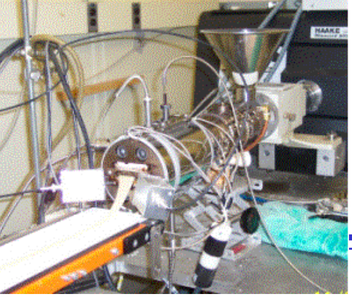


$$RC = \tau_{MW} = (2\pi f_{MW})^{-1}$$

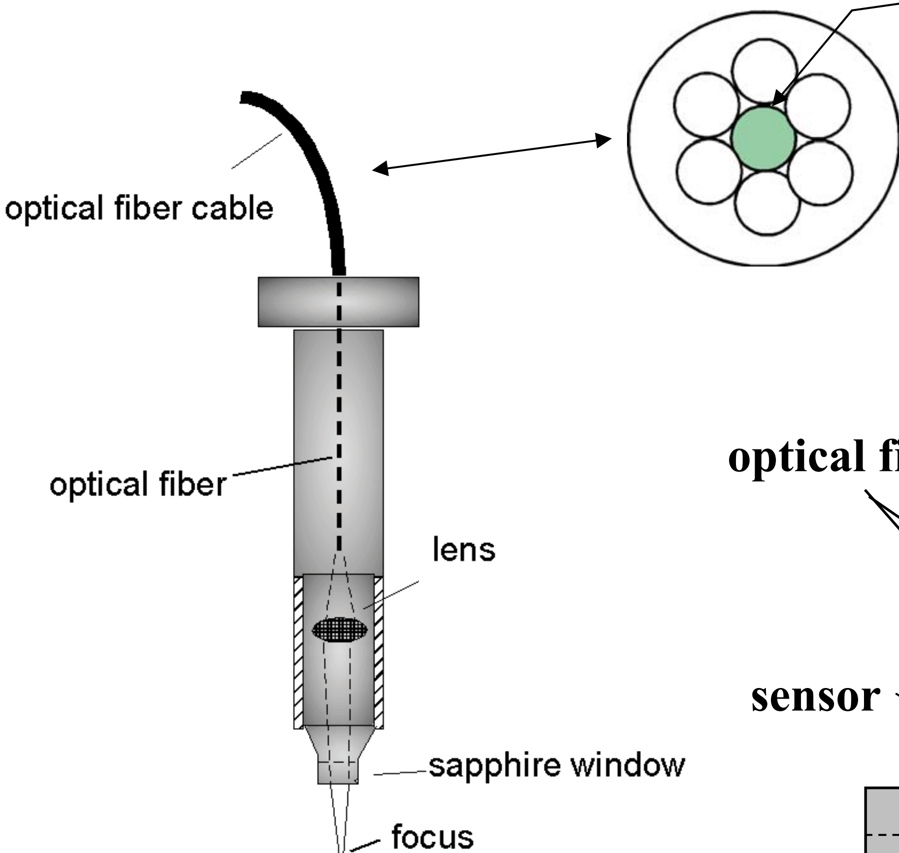
R = resistance of nylon (constant)

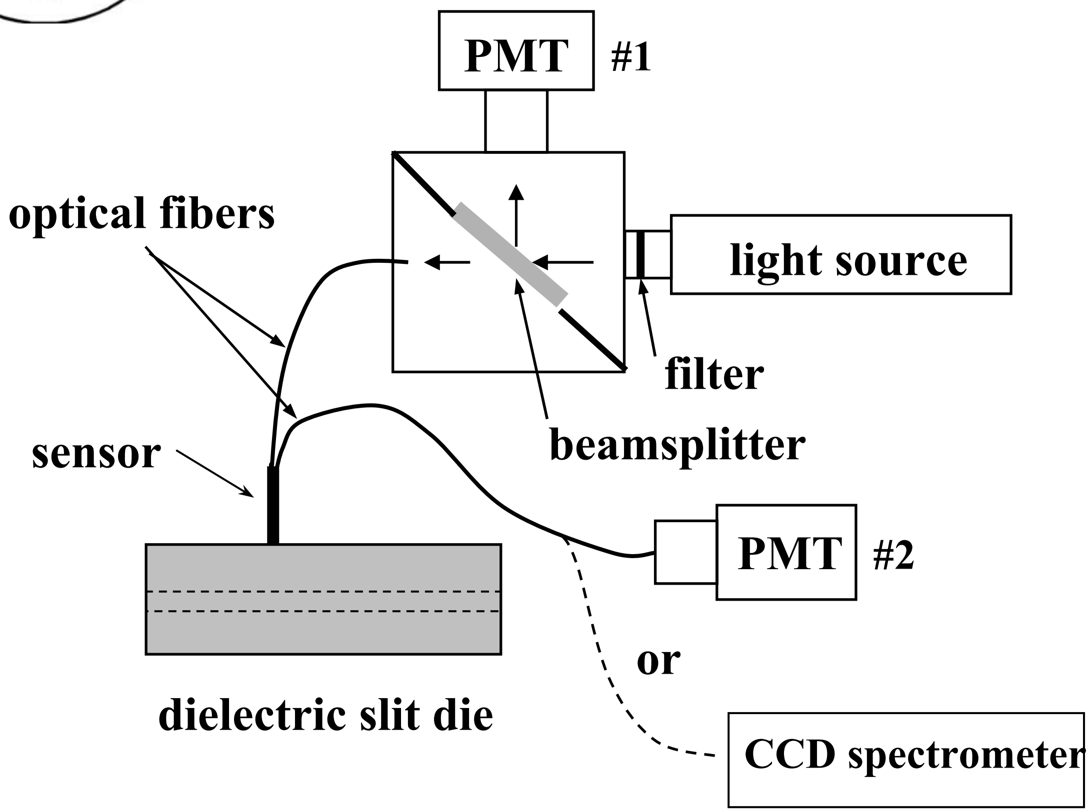
C = capacitance of clay particle (increases with exfoliation)

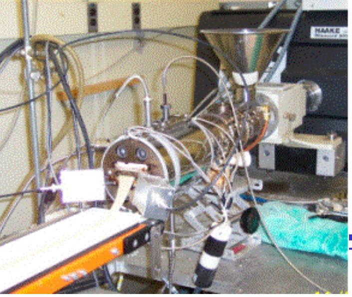
τ_{MW} large or f_{MW} small for exfoliated composite



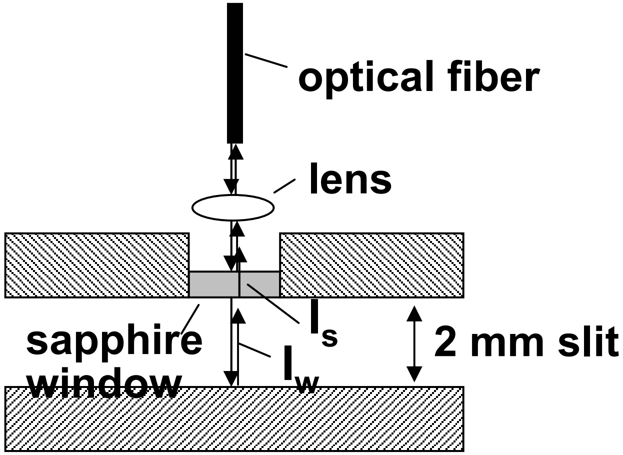
Compounding Nylon/Clay Composites: Optical Monitoring

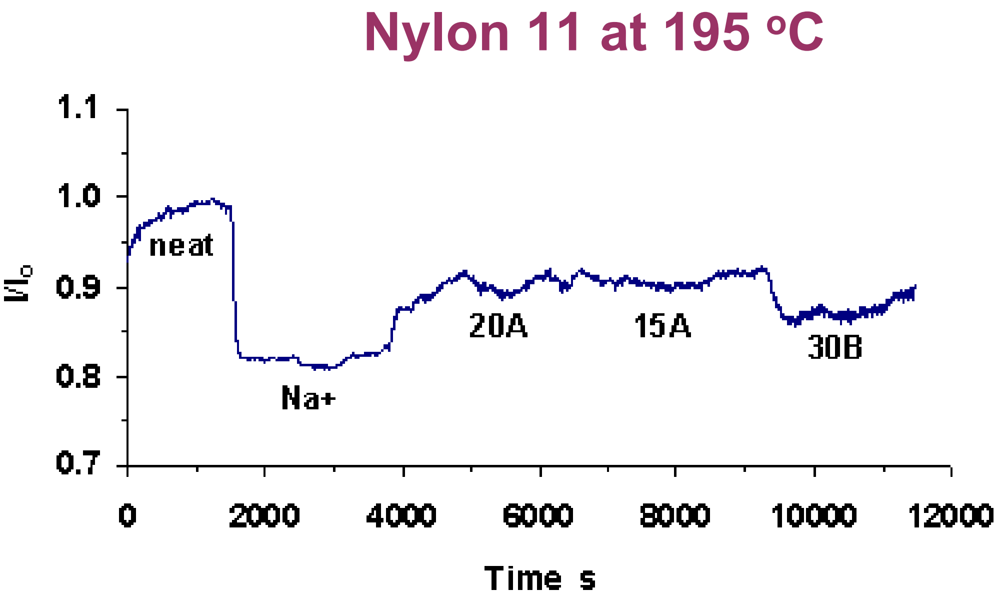


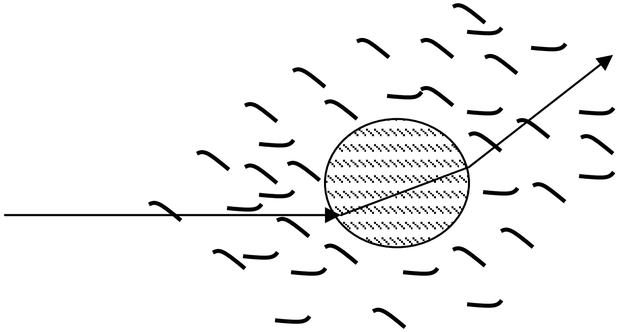


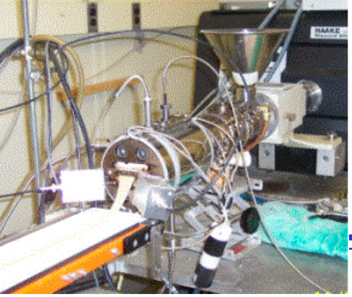


Compounding Nylon/Clay Composites: Optical Monitoring

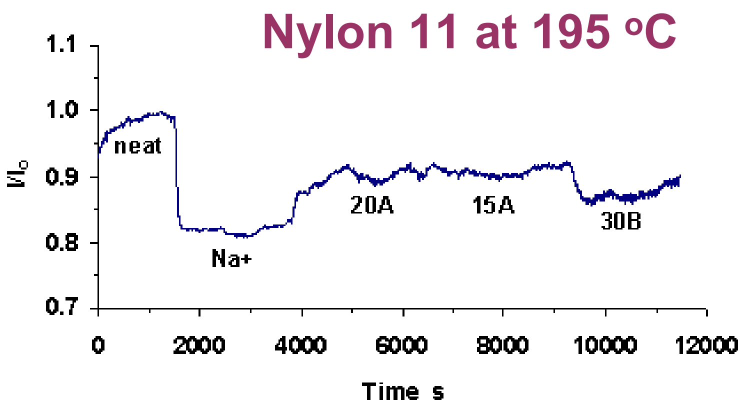






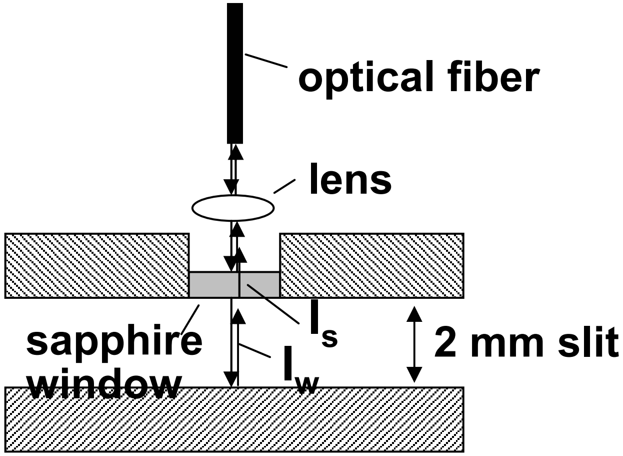


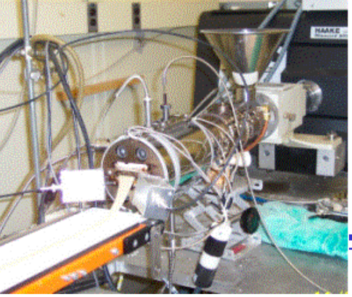
Compounding Nylon/Clay Composites: Optical Monitoring



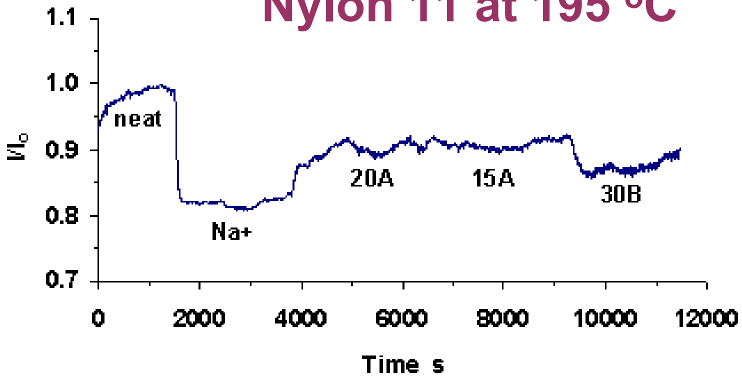
$$I_t = I_o e^{-\gamma\phi}$$

ϕ = volume fraction of aggregate



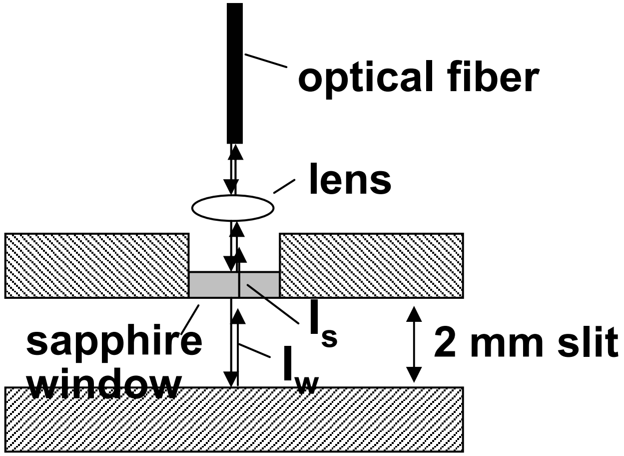


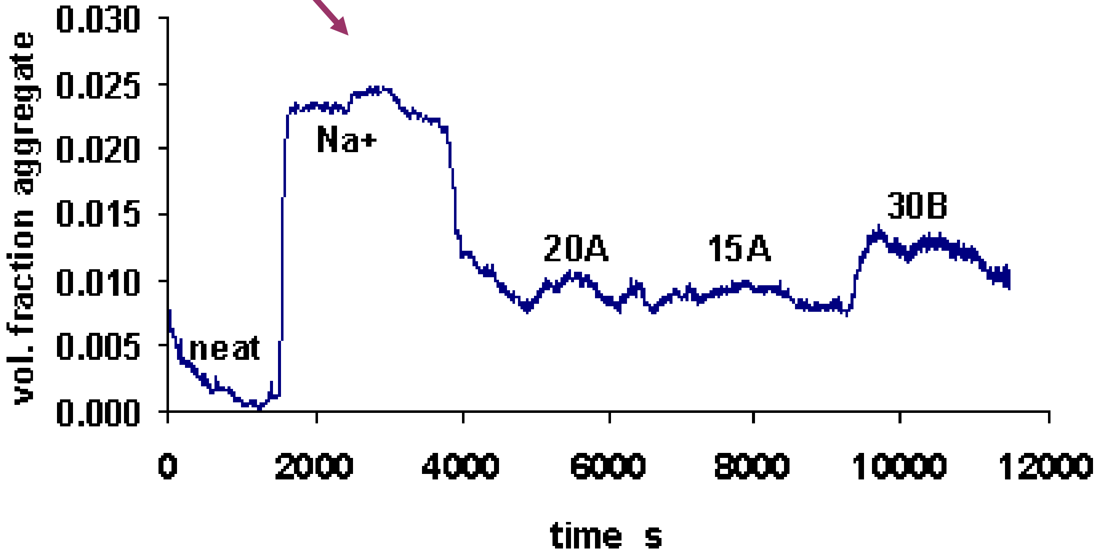
Compounding Nylon/Clay Composites: Optical Monitoring

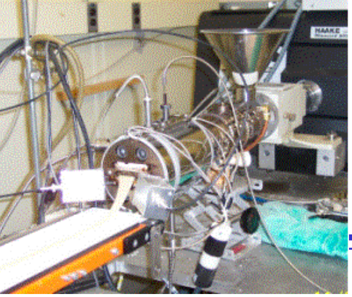


$$I_t = I_o e^{-\gamma\phi}$$

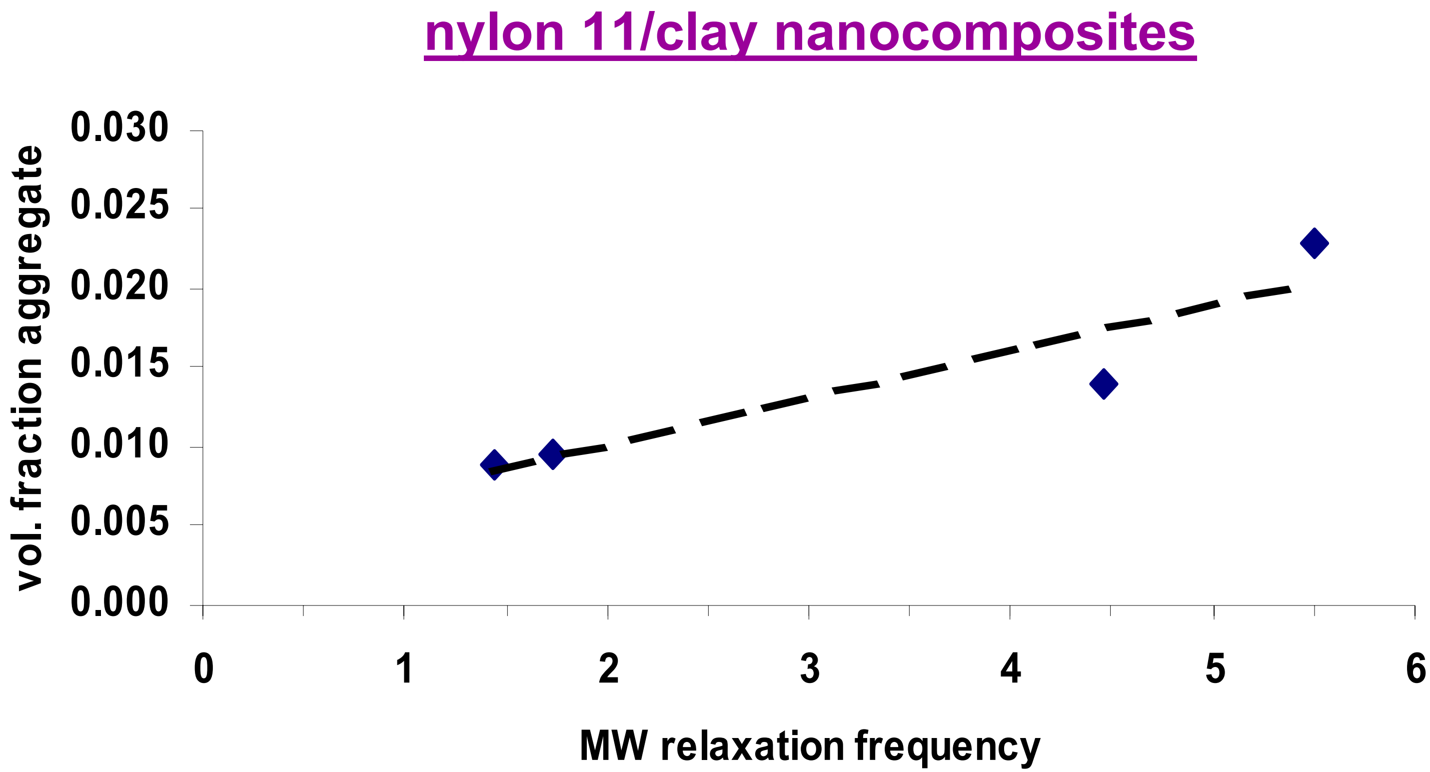
ϕ = volume fraction of aggregate

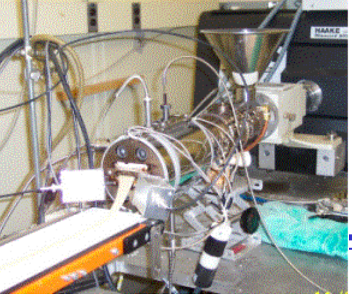




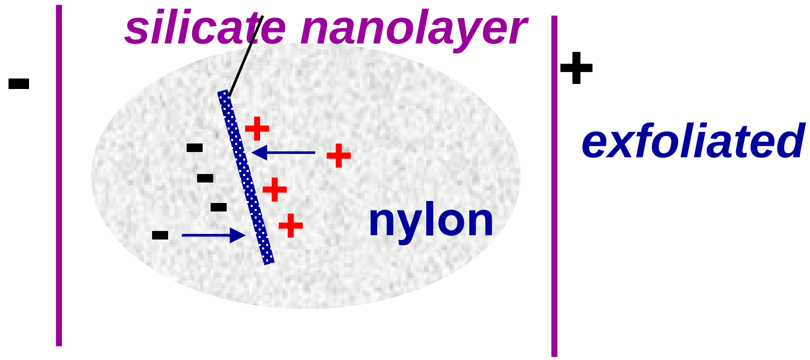


Compounding Nylon/Clay Composites
Extent of Exfoliation

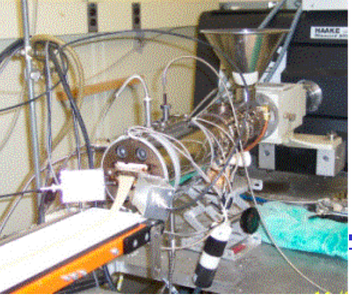




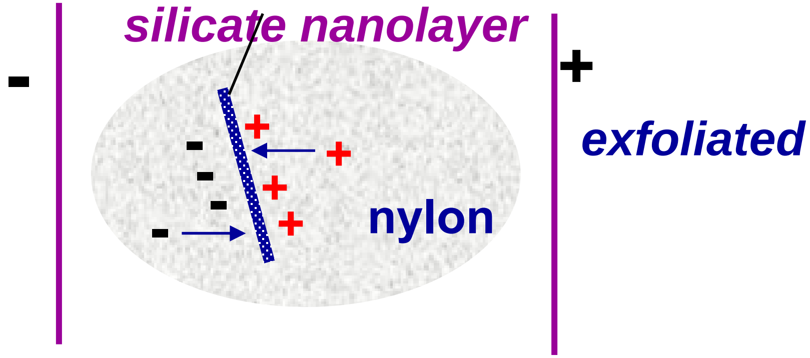
Compounding Nylon/Clay Composites Developing an Extent of Exfoliation Scale



Calculate time constant for charging capacitor



Compounding Nylon/Clay Composites Developing an Extent of Exfoliation Scale

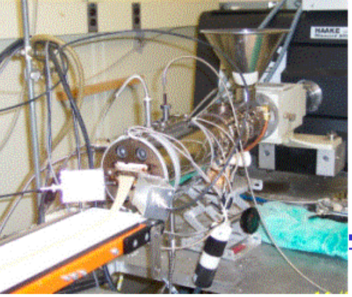


time constant: $RC = \tau_{MW}$ or $\rho\varepsilon = \tau_{MW}$

drift velocity: $bv = qE$ **where b = 6πηa (Stokes)**

Ohm's law: $nqv\,\rho = E$

Extent of Exfoliation: $$\boxed{\frac{n_o C}{n C_o} = \frac{n_o q^2 \tau_{MW}}{6\pi\varepsilon_o \eta a}}$$



Compounding Nylon/Clay Composites
Developing an Extent of Exfoliation Scale

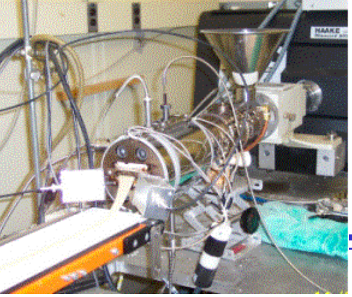
Extent of Exfoliation:

$$\boxed{\frac{n_o C}{n C_o} = \frac{n_o q^2 \tau_{MW}}{6\pi\varepsilon_o \eta a}}$$

η is molecular viscosity – obtain from diffusion constant or dielectric relaxation time

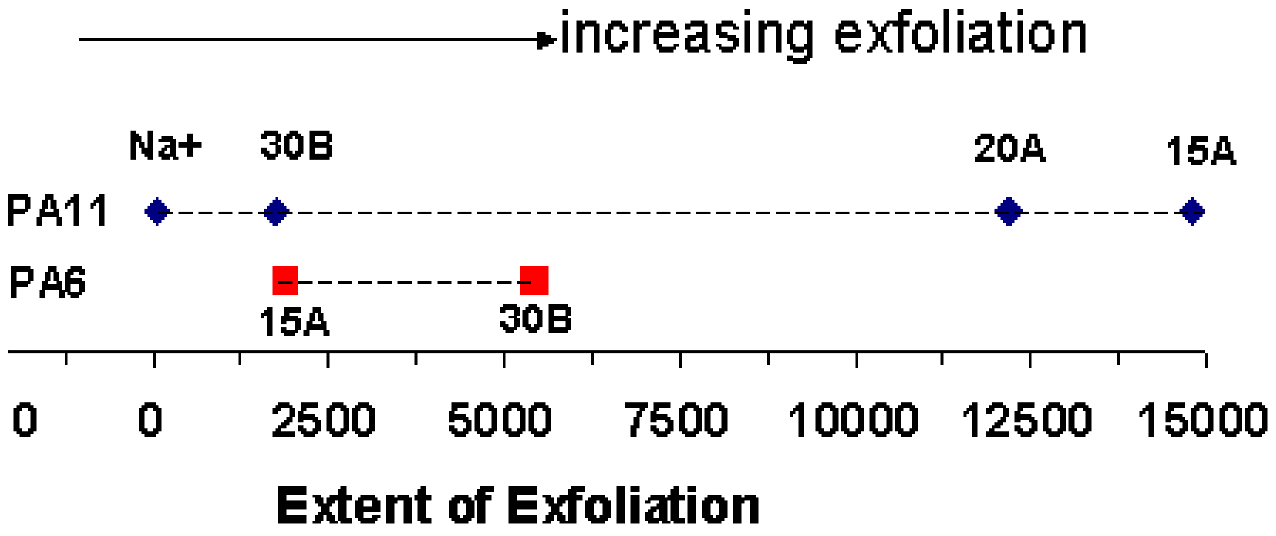
From dielectric measurements:

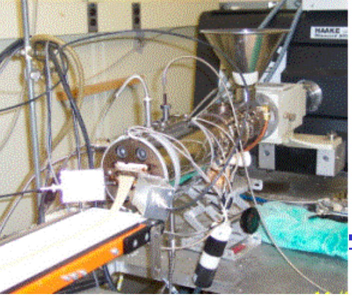
$$\tau_r = \frac{8\pi\eta a^3}{2kT}$$



An Extent of Exfoliation Scale

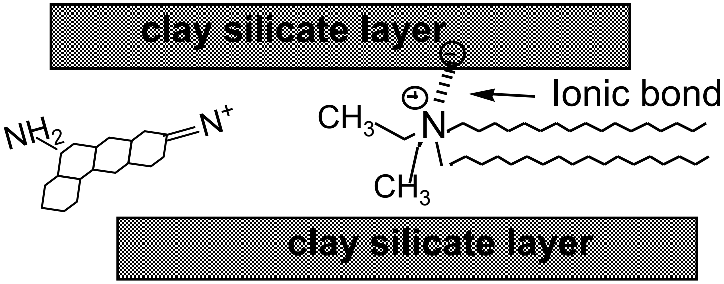
Use τ_r from γ relaxation of nylon:



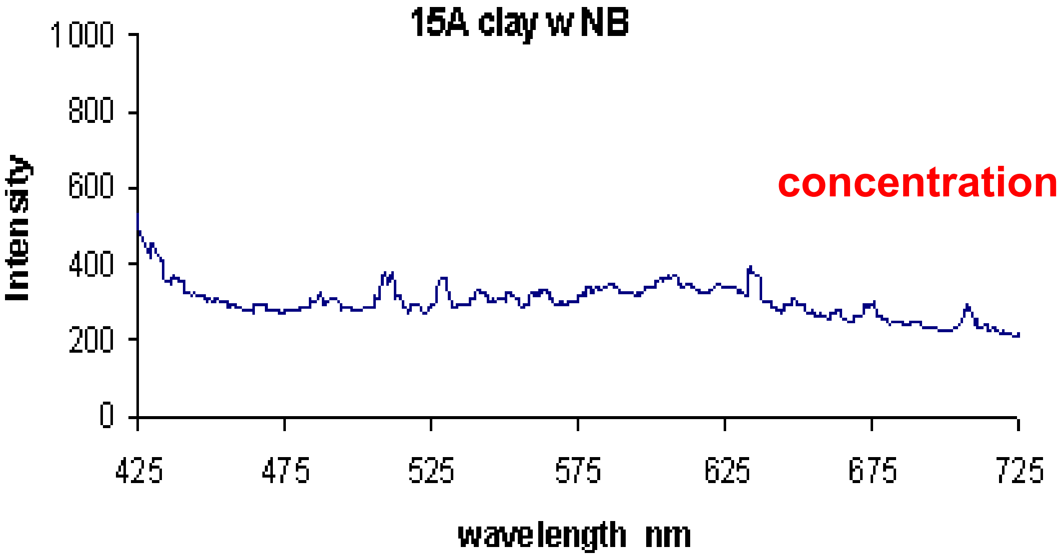


Compounding Nylon/Clay Composites: Fluorescence Monitoring

nile blue replaces 5% of surfactant by ion exchange

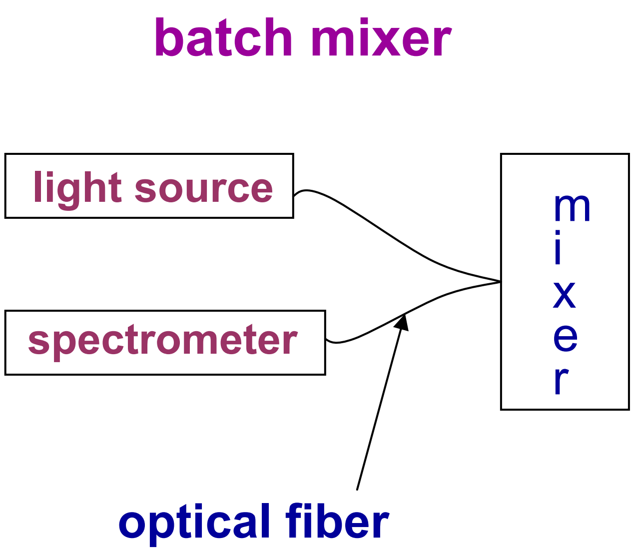


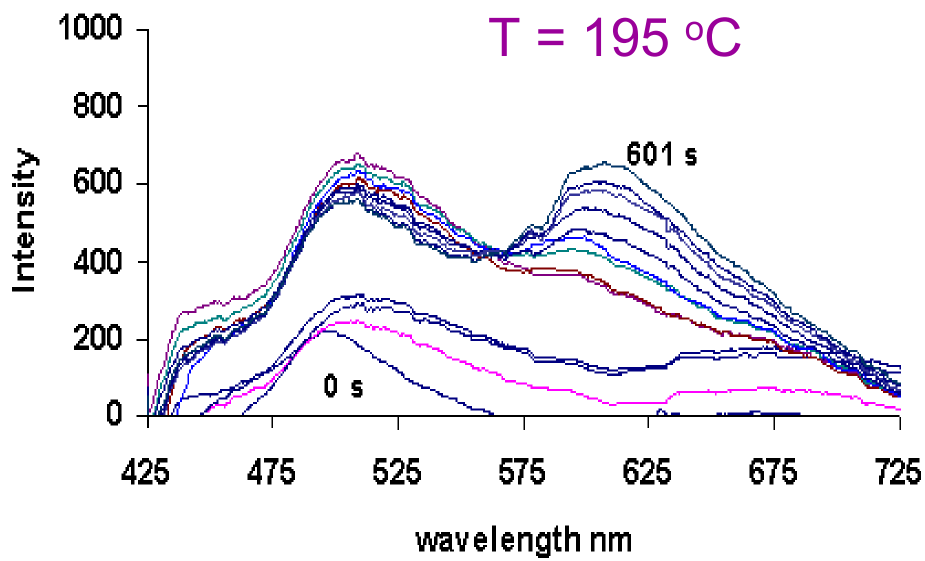
organo surfactant 15A

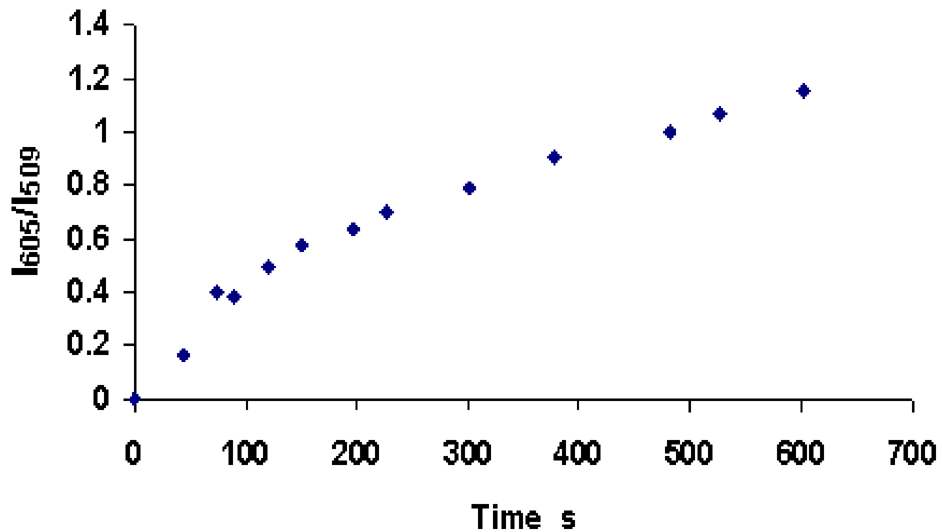


concentration quenching

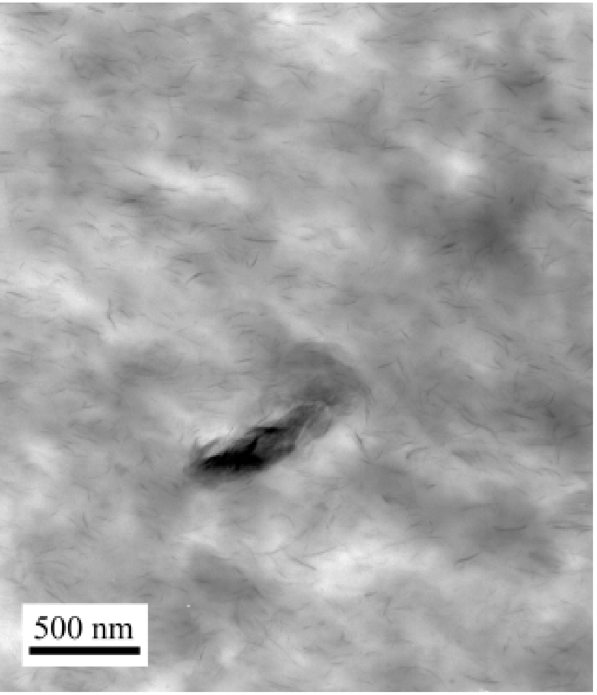
Compounding Nylon 11/15A nile blue dye



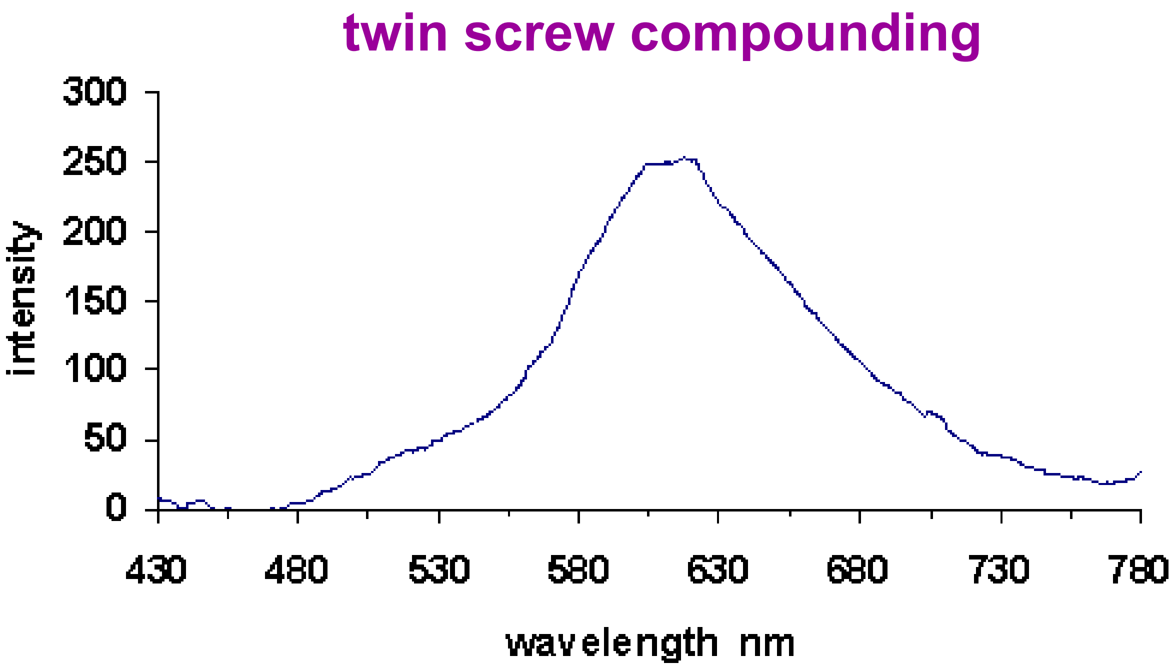


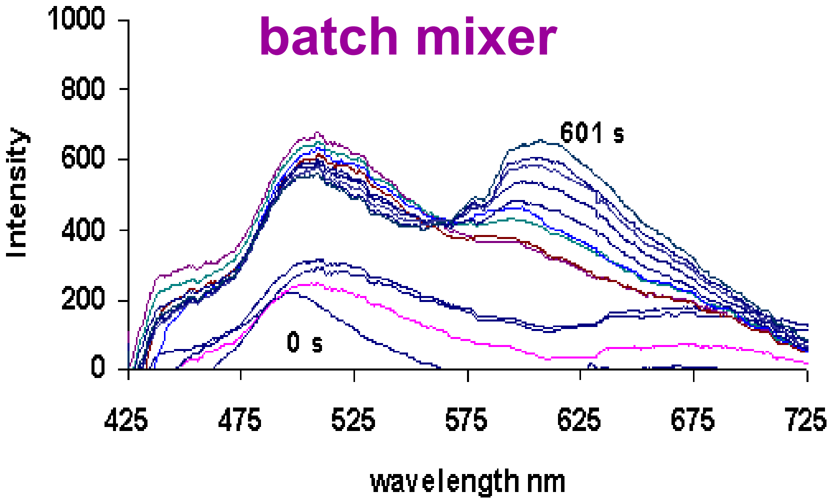


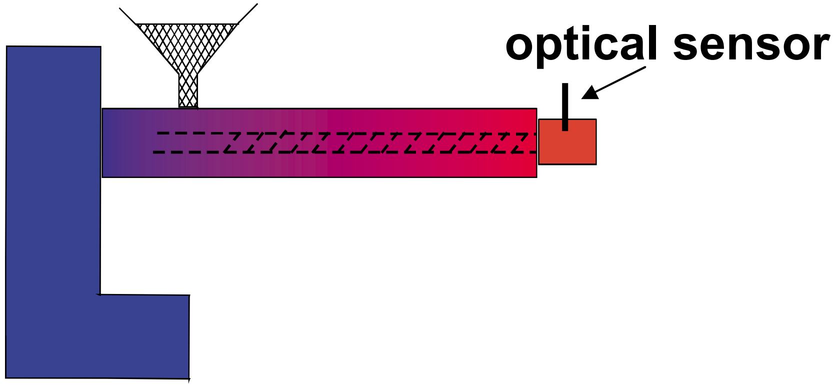
Compounding Nylon 11/15A nile blue

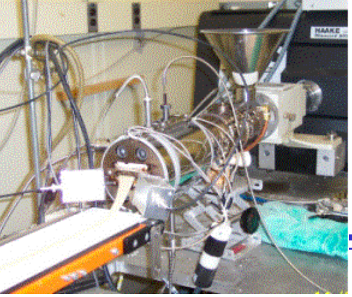


TEM from extrusion









Summary

- The NIST Dielectric Slit Die
- Extent of exfoliation in nylon/clay nanocomposites from
  - Dielectric
  - Optical transmission
  - Fluorescence
- Measuring Extent of Exfoliation is prerequisite

  for controlling exfoliation